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(54) **PHOTOELECTROCHEMICAL
PHOTOELECTRODE FOR WATER
SPLITTING CAPABLE OF SCALE-UP AND
WATER SPLITTING APPARATUS
INCLUDING THE SAME**

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(2013.01); *C25B 1/04* (2013.01); *C25B 1/55*
(2021.01)

(57) **ABSTRACT**

The present disclosure relates to a photoelectrochemical photoelectrode for water splitting, which includes a plate-type photoelectrode including a transparent electrode substrate and a photoanode layer disposed on the transparent electrode substrate, wherein the plate-type photoelectrode exists in a plural number, and the plural plate-type photoelectrodes are disposed in such a manner that the transparent electrode substrate of one photoelectrode may face the photoanode layer of the other photoelectrode, while being spaced apart from each other. In this manner, it is possible to scale-up the photoelectrochemical photoelectrode for water splitting, while providing improved water splitting performance.

Square electrode

<Side view>

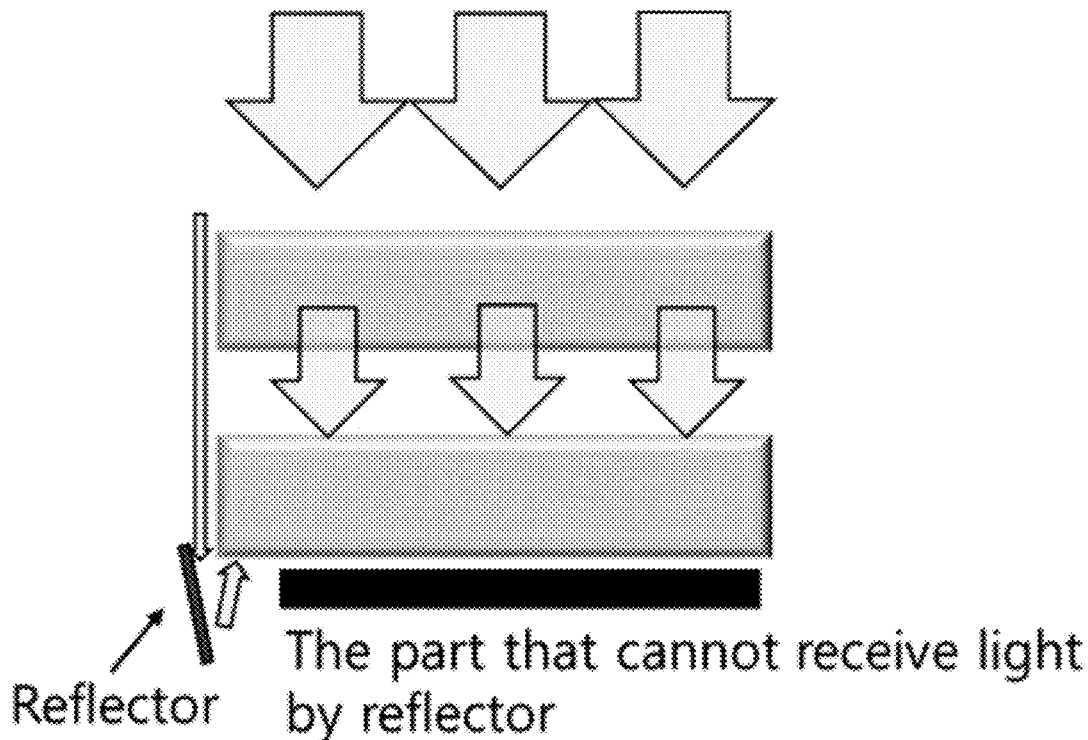


FIG. 1A

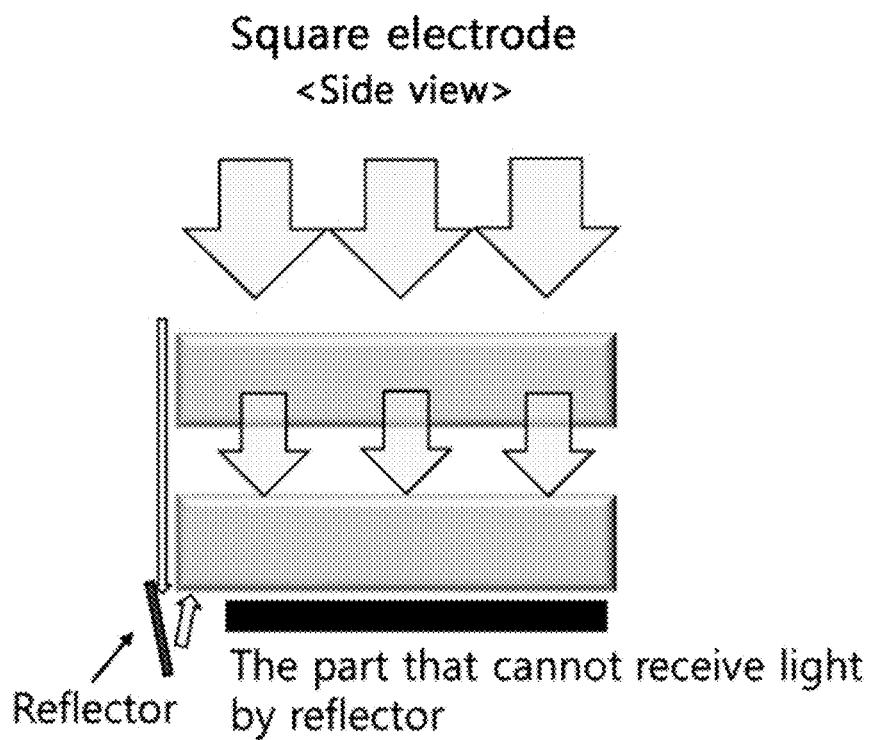


FIG. 1B

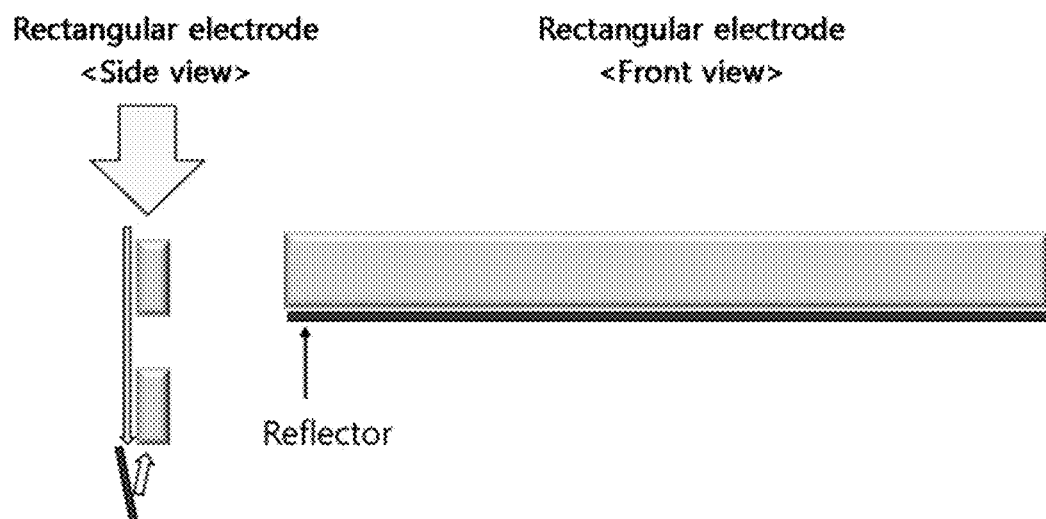


FIG. 2A

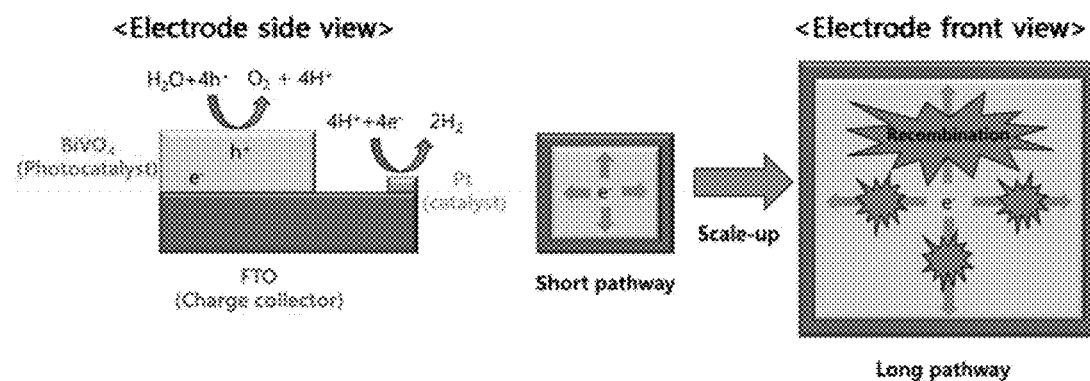


FIG. 2B

Rectangle type

<Front view>

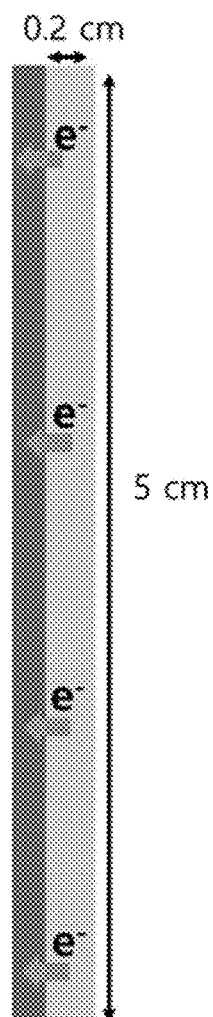


FIG. 3

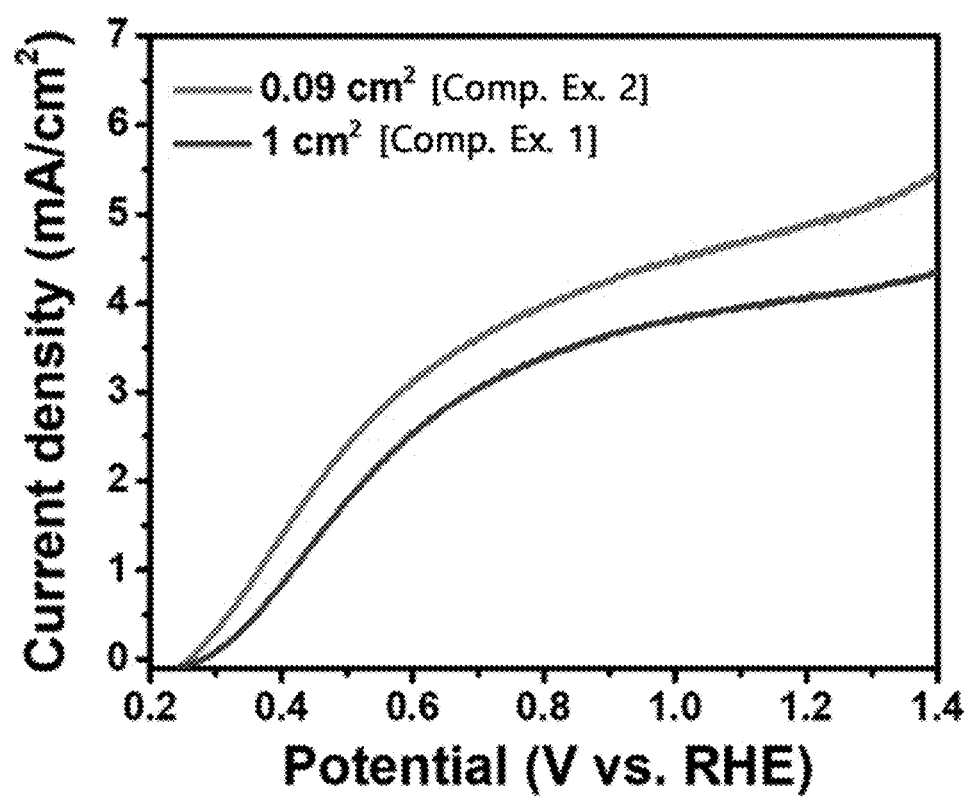


FIG. 4A

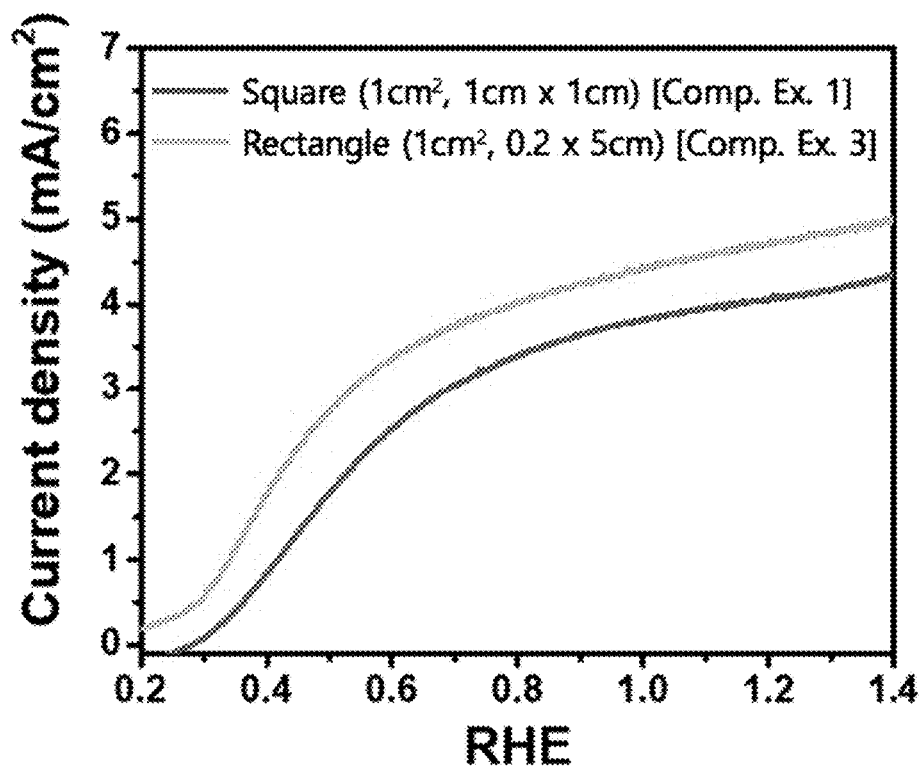


FIG. 4B

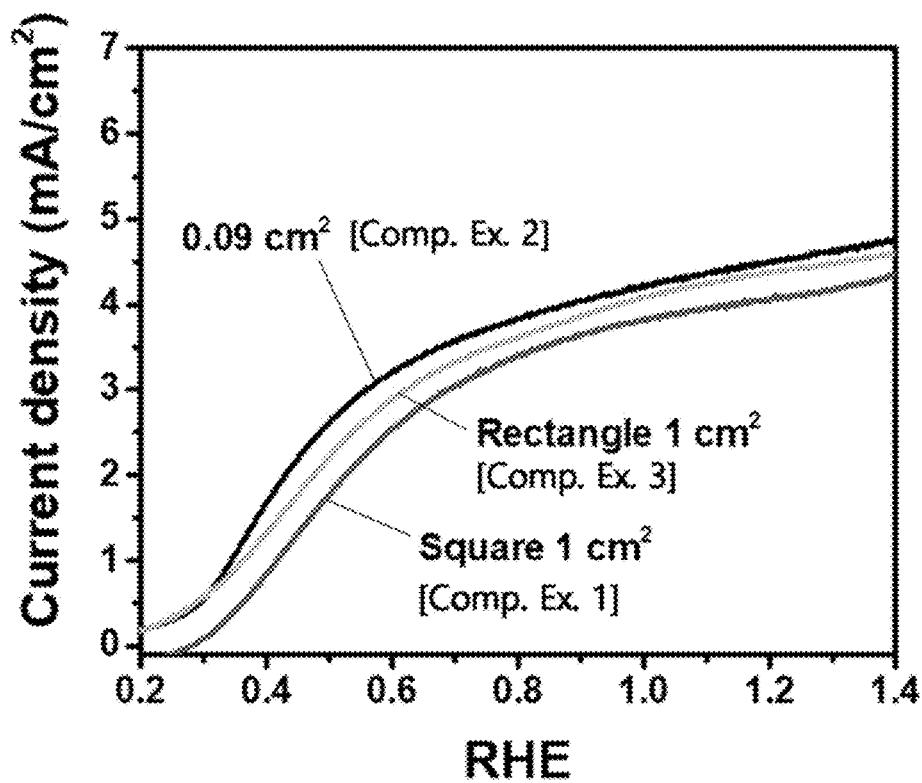


FIG. 5A

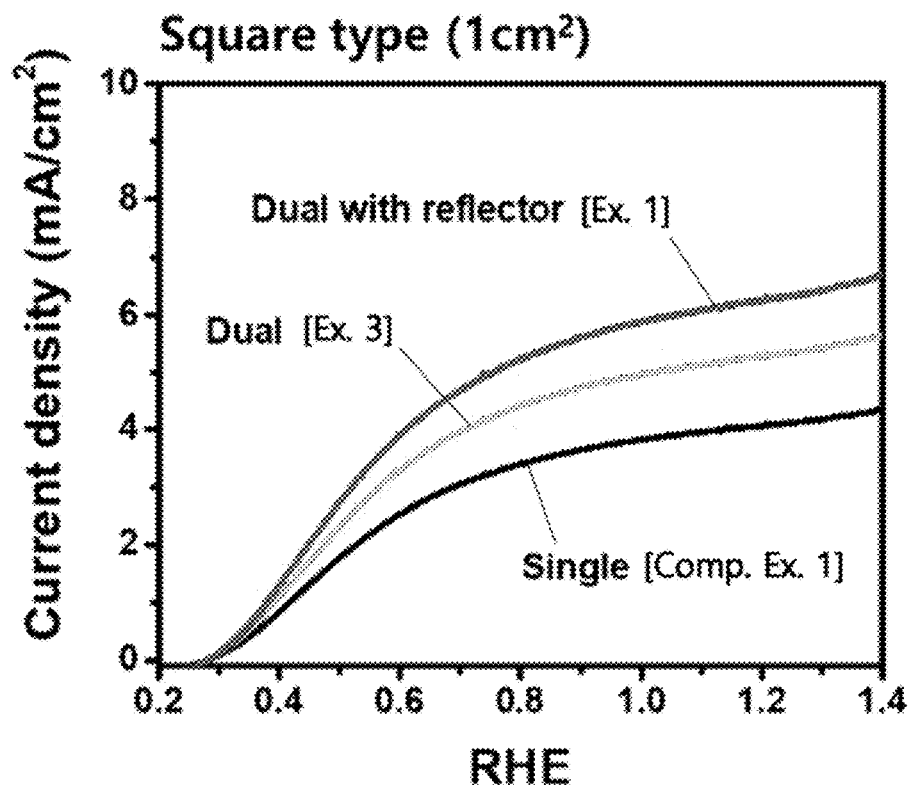


FIG. 5B

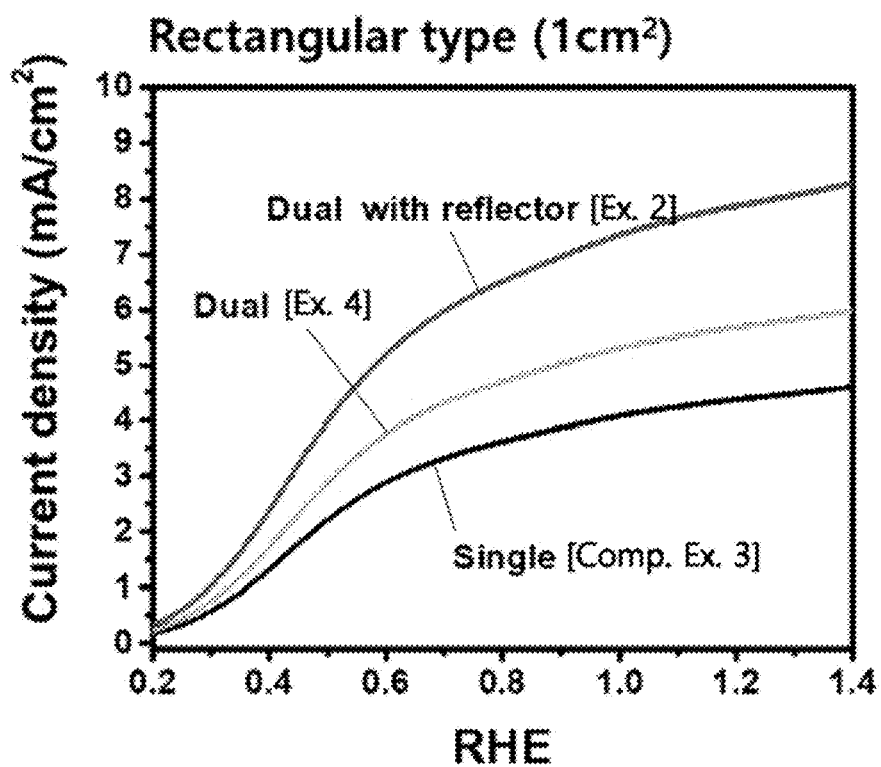


FIG. 5C

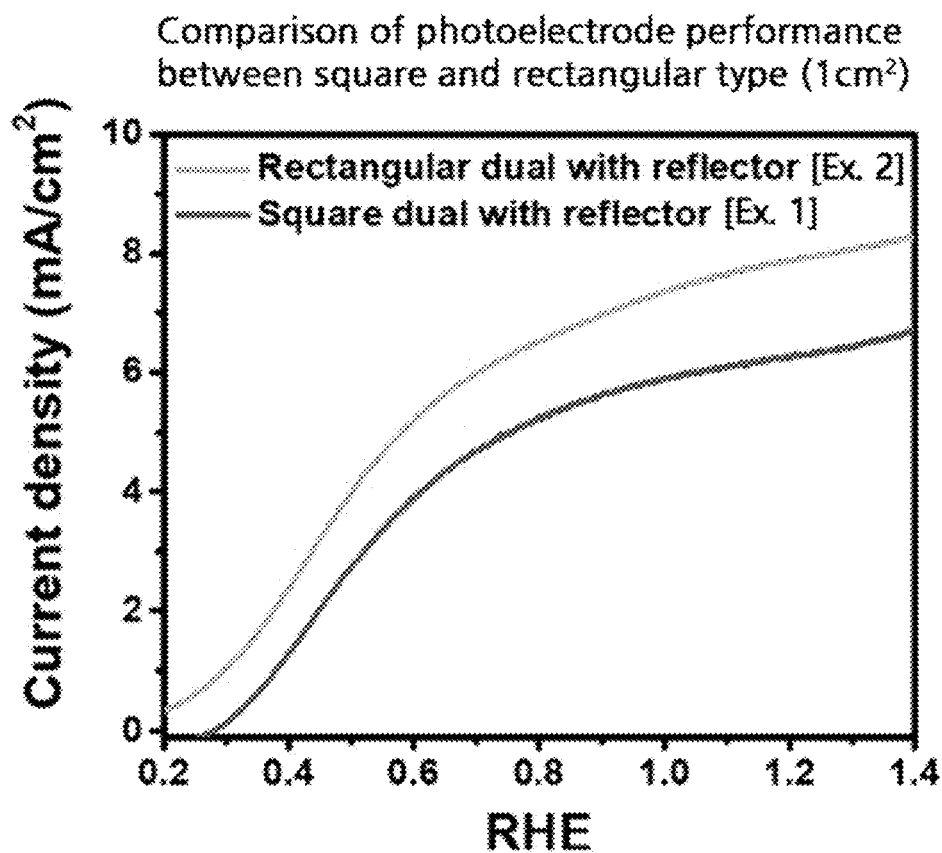


FIG. 6

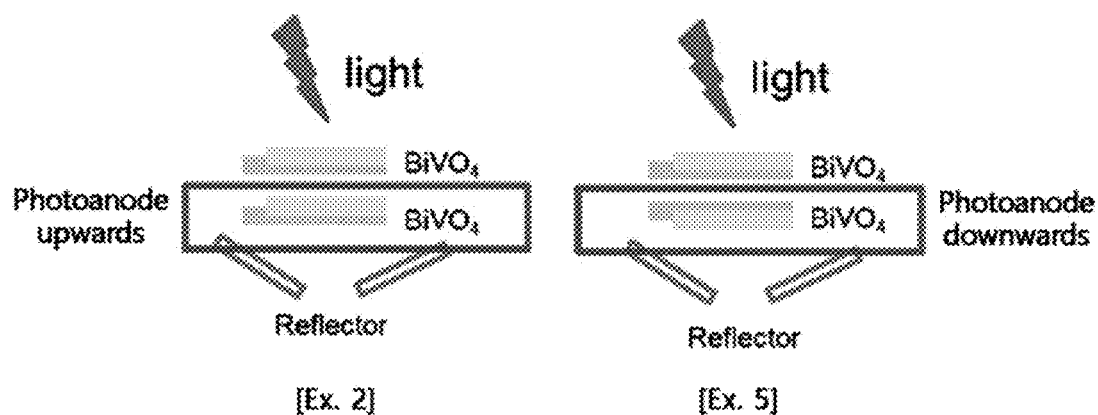


FIG. 7A

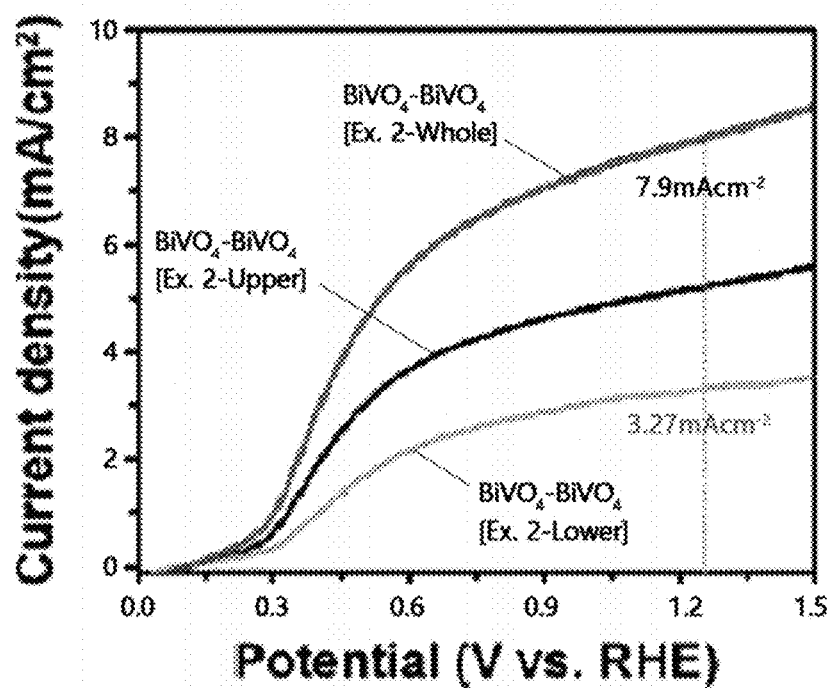


FIG. 7B

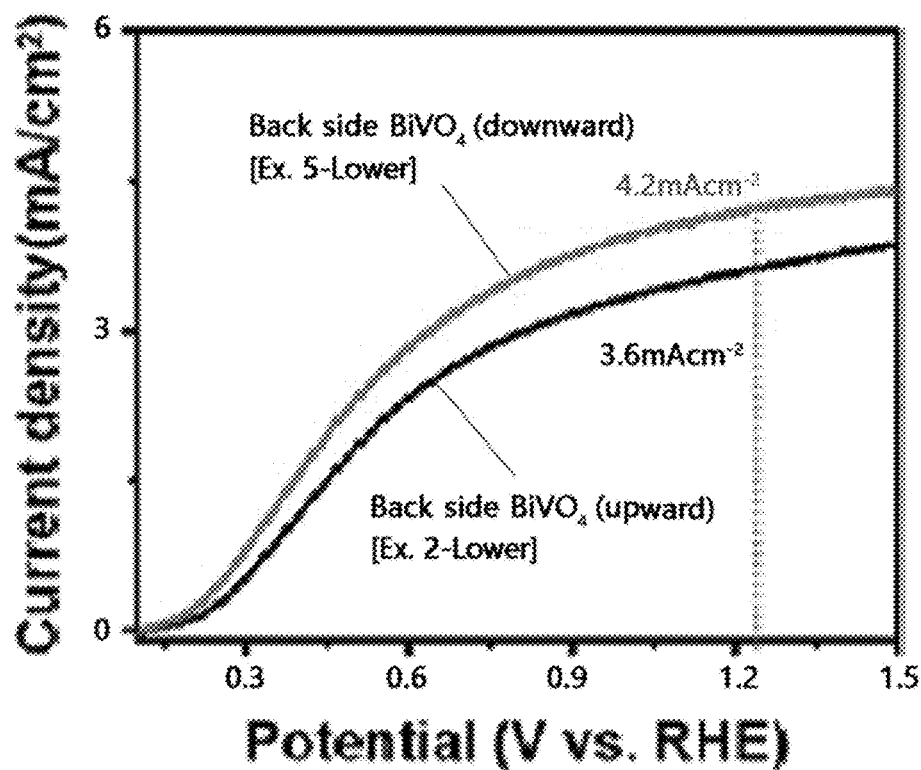


FIG. 7C

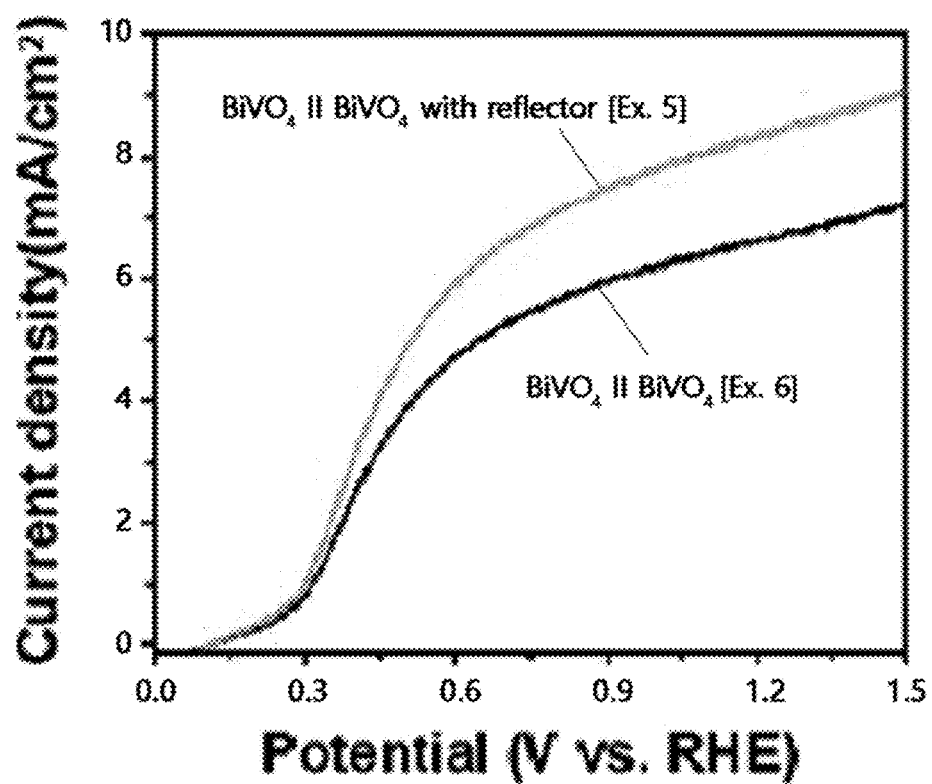


FIG. 8A

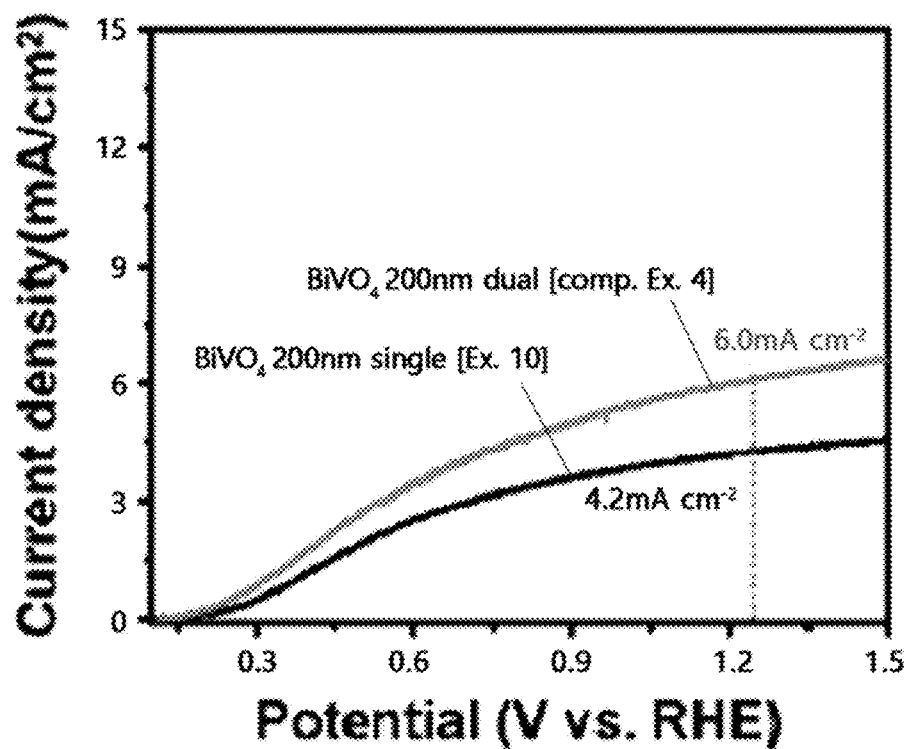


FIG. 8B

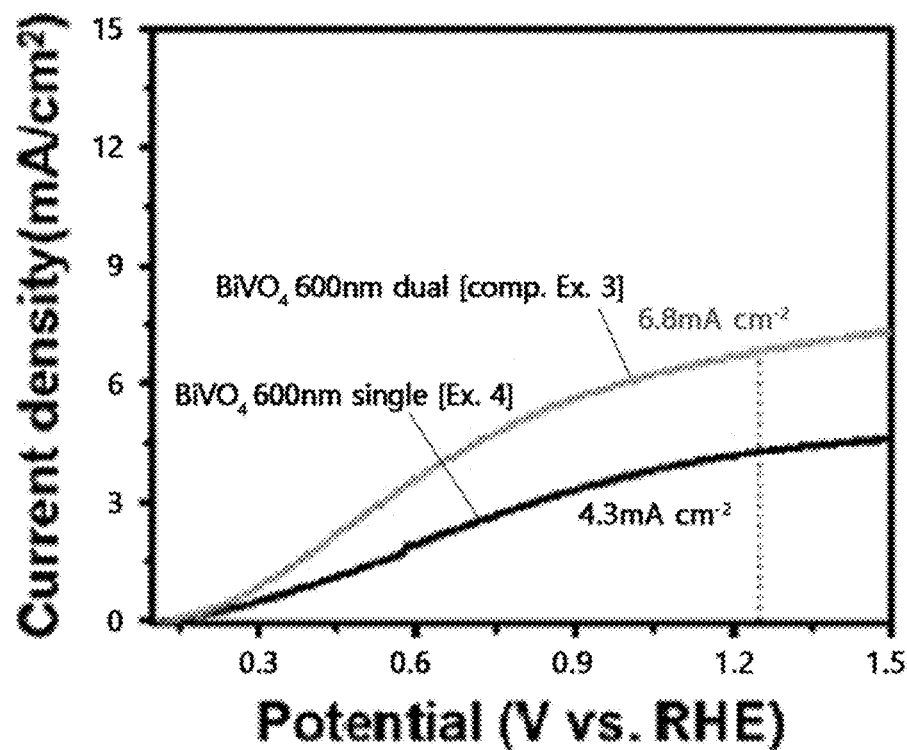


FIG. 8C

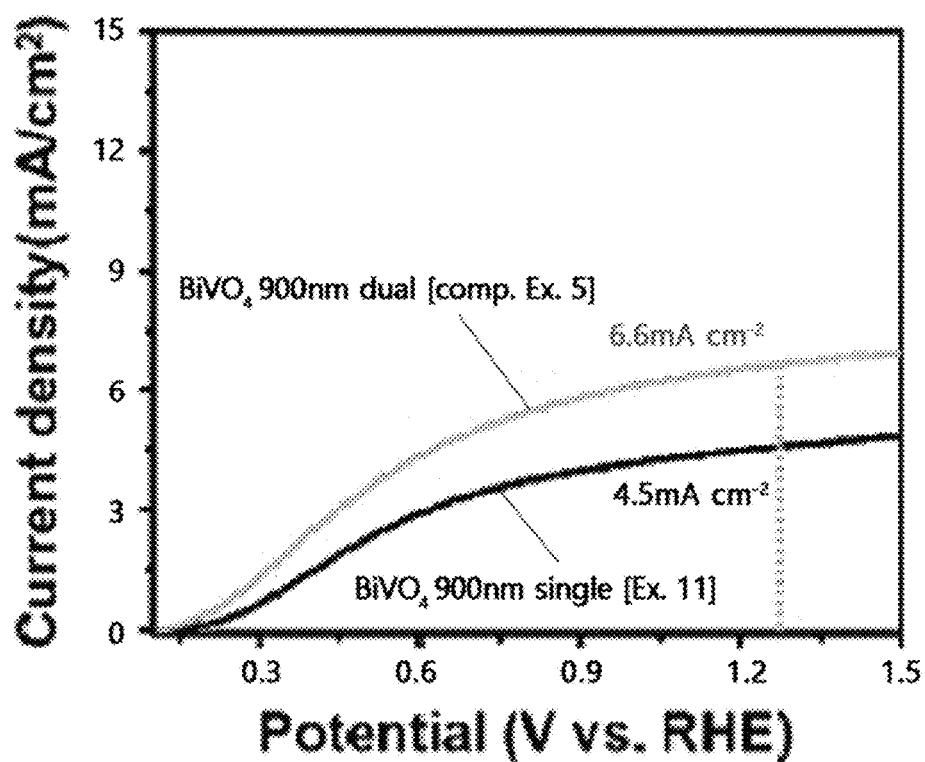


FIG. 8D

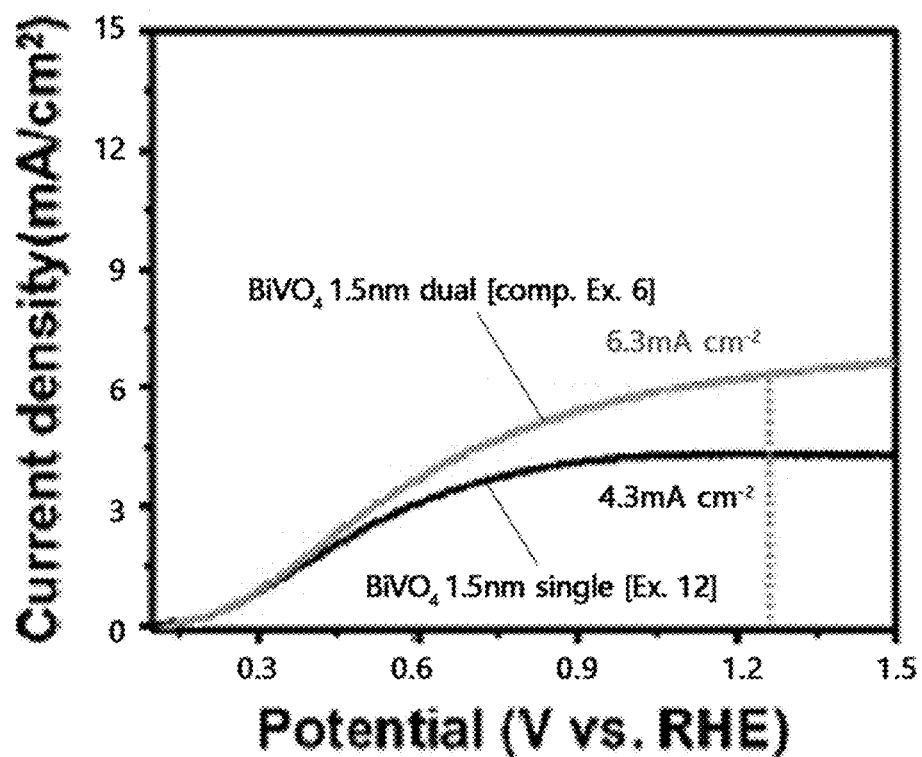


FIG. 9A

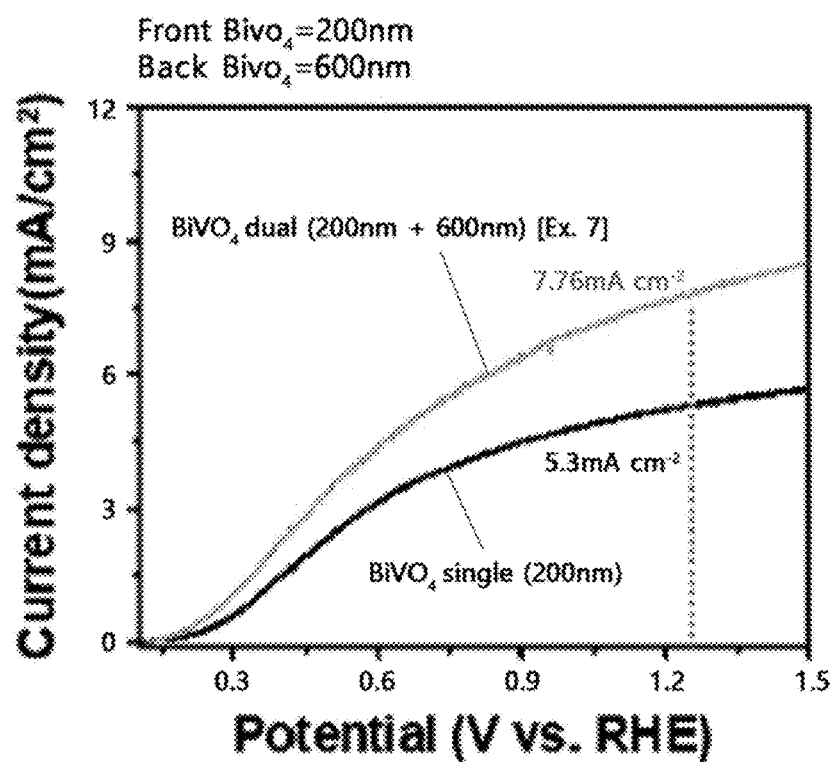


FIG. 9B

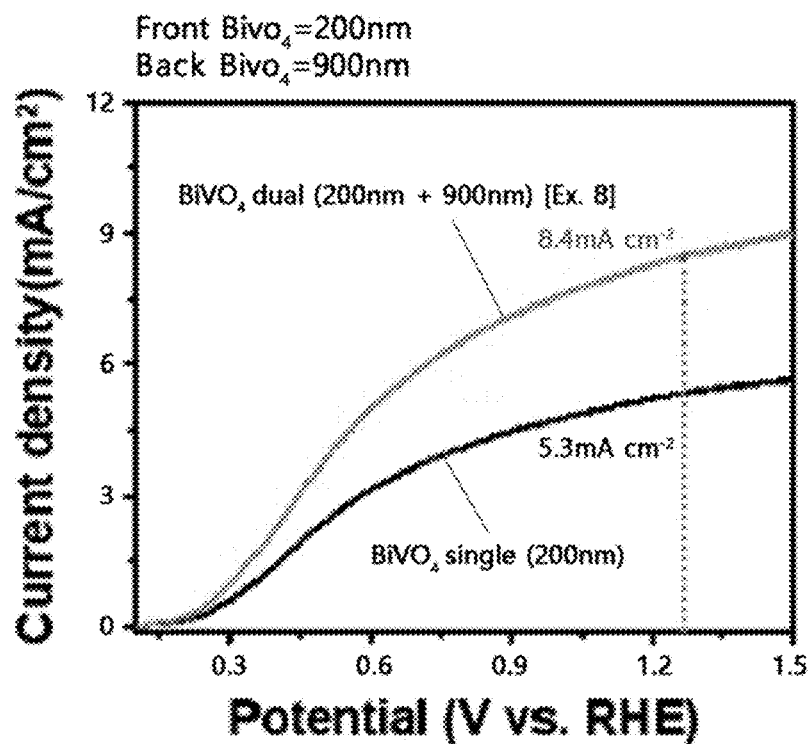
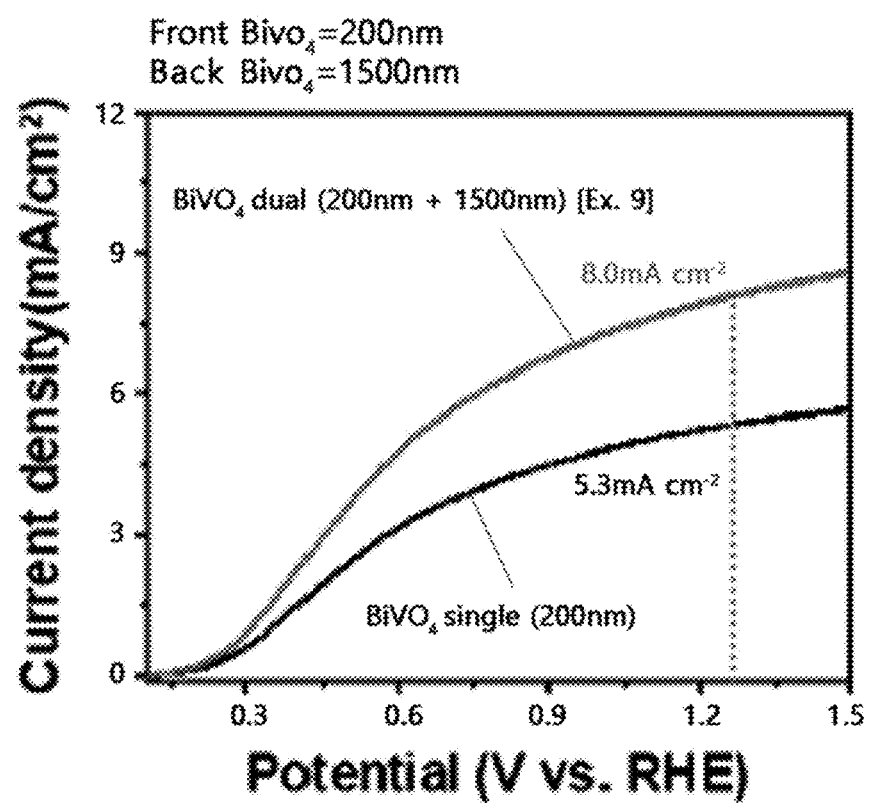


FIG. 9C



**PHOTOELECTROCHEMICAL
PHOTOELECTRODE FOR WATER
SPLITTING CAPABLE OF SCALE-UP AND
WATER SPLITTING APPARATUS
INCLUDING THE SAME**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

[0001] This application claims priority under 35 U.S.C. § 119 to Korean Patent Application No. 10-2020-0056367 filed on May 12, 2020 in the Korean Intellectual Property Office, the disclosure of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The following disclosure relates to a photoelectrochemical photoelectrode for water splitting, capable of scale-up, and a water splitting apparatus including the same. Particularly, the following disclosure relates to a photoelectrochemical photoelectrode, which has a modified design to allow scale-up and to increase water splitting efficiency, and a water splitting apparatus including the same.

BACKGROUND

[0003] A solution considering global warming, air pollution and energy supply is to find an eco-friendly energy source substituting for fossil fuels. The solar energy (173, 000 TW) supplied to the surface (water and ground) of the earth is 9600 times higher than the current total global energy consumption (17.91 TW in 2017). Although the solar energy is so large that it may be supplied to the solar system, technologies using, storing and acquiring the solar energy still remain a problem to be solved.

[0004] Some studies have been conducted about solar heat, solar cells, solar fuel, or the like, in order to use the solar energy. Currently, solar cells have been used widely. However, solar cells produce electricity, but there is a difficulty in storing the produced electricity. To solve this, a method for converting the solar energy into easily storable chemical energy and fuel has been given many attentions as an ideal method. Among various solar fuel methods, hydrogen gas (H_2) obtained through water splitting using the solar energy has been given many attentions as a promising fuel.

[0005] Hydrogen gas has a higher gravimetric heating value (141.9 MJ kg^{-1}) as compared to the conventionally used fossil fuels (methane 55.5 MJ kg^{-1} , gasoline 47.5 MJ kg^{-1} , diesel 44.8 MJ kg^{-1} , and methanol 20.0 MJ kg^{-1}), and the byproducts generated by firing hydrogen is merely water. However, since most hydrogen gas is obtained by reforming fossil fuels, a large amount of CO_2 is generated. Therefore, there is a need for constructing a hydrogen gas production system which can be sustained at reasonable costs, generates a low amount of carbon and can be realized in an industrial scale. It is highly likely that photoelectrochemical (PEC) water splitting becomes a method for producing hydrogen gas using the solar energy.

[0006] Studies about PEC water splitting have covered largely development of materials, physical chemistry and systems. However, large-scale PEC water splitting systems have not been covered frequently. This is a process to be treated by PEC water splitting technology someday for the purpose of realizable production of hydrogen gas.

[0007] The first problem in scale-up is that when the size of a photoelectrode is increased, the total efficiency is reduced due to the sheet resistance of a substrate. The second problem is that scale-up requires a fabrication method different from the fabrication in a laboratory scale, and the spatial defects generated herein and an increase in total ohmic resistance may reduce the efficiency of an up-scaled photoelectrode. The last problem is separation of the resultant fuel (H_2 : hydrogen gas, O_2 : oxygen gas). In general, a membrane separator is used for fuel separation, but this is covered merely in several PEC studies. Moreover, such studies have reported that use of a membrane separator causes high energy loss. Therefore, a change in PEC scale in a laboratory scale may cause reduction of the total PEC efficiency due to the above-mentioned problems. Under these circumstances, there is a need for a technology capable of realizing scale-up, while minimizing the reduction of the efficiency.

SUMMARY

[0008] The present disclosure is designed to solve the problems of the related art, and an embodiment of the present disclosure is directed to providing a photoelectrochemical photoelectrode for water splitting, which can realize scale-up, while not causing a decrease in photoelectrochemical water splitting efficiency through the modification of a design.

[0009] In one aspect of the present disclosure, there is provided a photoelectrochemical photoelectrode for water splitting, which includes a plate-type photoelectrode including a transparent electrode substrate and a photoanode layer disposed on the transparent electrode substrate, wherein the plate-type photoelectrode exists in a plural number, and the plural plate-type photoelectrodes are spaced apart from each other by a predetermined interval so that they may be disposed face-to-face.

[0010] The photoelectrochemical photoelectrode may further include a reflector which reflects the light transmitted through all of the plural photoelectrodes toward a rear photoelectrode side opposite to a front photoelectrode receiving light irradiation directly, upon the light irradiation.

[0011] The reflector may be disposed in the shape of a plate along one side of the rear photoelectrode.

[0012] The reflector may be installed to form an angle of $3-45^\circ$ with the rear photoelectrode.

[0013] The reflector may include any one material selected from glass, crystal, halite, metals and polymers.

[0014] The photoelectrode may include two plate-type photoelectrodes.

[0015] The two plate-type photoelectrodes may be disposed in such a manner that the surfaces of the transparent electrode substrates having no photoanode layer may face each other.

[0016] The photoanode layers disposed on each of the two plate-type photoelectrodes may have the same thickness and may be formed to have a thickness of 500-700 nm.

[0017] The photoanode layers disposed on each of the two plate-type photoelectrodes may have a different thickness, wherein the front photoanode layer receiving light irradiation directly may have a thickness of 50-450 nm, and the remaining rear photoanode layer may have a thickness of 600-1500 nm.

[0018] The two plate-type photoelectrodes may be disposed in such a manner that they may be spaced apart from each other by an interval of 0.1-1.0 mm.

[0019] The plate-type photoelectrode may be a square plate-type photoelectrode or a rectangular plate-type photoelectrode.

[0020] The photoanode layer may have an area of 0.1-100 cm².

[0021] The photoanode layer may have a ratio of width and length of 1:1-1:100.

[0022] The transparent electrode substrate may be any one selected from FTO (Fluorine doped Tin Oxide), ZnO (Zinc Oxide), ITO (Indium Tin Oxide), AZO (Antimony Zinc Oxide), GZO (Gallium doped Zinc Oxide), IZO (Indium Zinc Oxide), and IGZO (Indium gallium zinc oxide).

[0023] The photoanode layer may include any one selected from bismuth vanadate (BiVO₄), hematite (Fe₂O₃), and tungsten oxide (WO₃).

[0024] In another aspect of the present disclosure, there is provided a water splitting apparatus including the photoelectrochemical photoelectrode for water splitting.

[0025] In the photoelectrochemical photoelectrode for water splitting according to the present disclosure, plural photoelectrodes are disposed in the longitudinal direction, a reflector is introduced to the rear surface, the size, the shape, the position and the thickness of a photoanode in the photoelectrode are controlled to transfer the light effectively to the whole photoelectrode, and the migration distance of the electrons generated by the light is reduced to maximize the water splitting performance. In this manner, it is possible to accomplish scale-up, while improving the water splitting performance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] FIGS. 1A and 1B show the schematic structure of a square plate-type photoelectrode and that of a rectangular plate-type photoelectrode according to an embodiment of the present disclosure.

[0027] FIGS. 2A and 2B show the schematic structure of the photoelectrode according to

[0028] Comparative Examples 1 and 2 and that of the photoelectrode according to Comparative Example 3.

[0029] FIG. 3 shows the result of water splitting performance analysis depending on the area of a photoelectrochemical photoelectrode according to Test Example 1. FIGS. 4A and 4B show the result of water splitting performance analysis depending on the shape of a photoelectrode according to Test Example 2.

[0030] FIGS. 5A to 5C show the result of analyzing the effect of a photoelectrode depending on the number of photoelectrodes, shape thereof and the presence of a reflector according to Test Example 3.

[0031] FIG. 6 shows the result of structural comparison between the photoelectrode according to Example 2 and the photoelectrode according to Example 5, wherein the photoanode of the lower electrode is formed at the side opposite to each other in Examples 1 and 5.

[0032] FIGS. 7A to 7C show the result of water splitting performance analysis depending on the position of the photoanode according to Test Example 4.

[0033] FIGS. 8A to 8D show the result of water splitting performance analysis depending on the thickness of the photoanode according to Test Example 5.

[0034] FIGS. 9A to 9C show the result of water splitting performance analysis depending on a change in thickness of the upper and lower photoanodes according to Test Example 6.

DETAILED DESCRIPTION OF EMBODIMENTS

[0035] Hereinafter, various aspects and embodiments of the present disclosure will be explained in more detail. Exemplary embodiments now will be described more fully hereinafter with reference to the accompanying drawings, in which exemplary embodiments are shown. The present disclosure may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth therein. In the description, details of well-known features and techniques may be omitted to avoid unnecessarily obscuring the presented embodiments.

[0036] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the present disclosure. As used herein, the singular forms “a”, “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. Furthermore, the use of the terms a, an, etc. does not denote a limitation of quantity, but rather denotes the presence of at least one of the referenced item. It will be further understood that the terms “comprises” and/or “comprising”, or “includes” and/or “including” when used in this specification, specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or groups thereof.

[0037] FIGS. 1A and 1B show the schematic structure of a square plate-type photoelectrode and that of a rectangular plate-type photoelectrode according to an embodiment of the present disclosure. Hereinafter, the photoelectrochemical photoelectrode for water splitting according to the present disclosure will be explained in detail with reference to FIGS. 1A and 1B.

[0038] The photoelectrochemical photoelectrode for water splitting according to the present disclosure includes a plate-type photoelectrode including a transparent electrode substrate and a photoanode layer disposed on the transparent electrode substrate.

[0039] The plate-type photoelectrode exists in a plural number, and the plural plate-type photoelectrodes are spaced apart from each other by a predetermined interval so that they may be disposed face-to-face. In this manner, the light input to one photoelectrode may transmit through the transparent electrode substrate and arrive at another photoelectrode.

[0040] Preferably, the photoelectrochemical photoelectrode may further include a reflector which reflects the light transmitted through all of the plural photoelectrodes toward a rear photoelectrode side opposite to a front photoelectrode receiving light irradiation directly, upon the light irradiation.

[0041] As shown in FIGS. 1A and 1B, the reflector may be disposed in the shape of a plate along one side of the rear photoelectrode, wherein the reflector is installed preferably to form an angle of 3-45° with the rear photoelectrode.

[0042] Meanwhile, the reflector may be made of any one material selected from glass, crystal, halite, metals and polymers.

[0043] The plate-type reflector is merely an example, and the scope of the present disclosure is not limited thereto. The reflector is used for the purpose of increasing the light utilization efficiency by irradiating the light transmitted through all of the plural photoelectrodes toward a rear photoelectrode side which does not receive light irradiation directly. Therefore, any reflectors using various positions, shapes and materials may be applied, as long as they can accomplish the above-described objects and cause no disturbance in use of the photoelectrode.

[0044] The photoelectrode preferably includes two plate-type photoelectrodes. When only one photoelectrode is used, a water splitting apparatus using the photoelectrode shows low water splitting performance. When three or more photoelectrodes are used, the light efficiency per photoelectrode is degraded, which is not preferred in cost efficiency.

[0045] The two plate-type photoelectrodes may be disposed in such a manner that they may be spaced apart from each other by an interval of 0.1-1.0 mm, particularly 0.2-0.5 mm. When the interval is less than 0.1 mm, the transparent electrode substrate of one photoelectrode may be in contact with the photoanode of the other photoelectrode.

[0046] When the interval is larger than 1.0 mm, the volume occupied by the photoelectrodes is increased undesirably.

[0047] The two plate-type photoelectrodes may be disposed in such a manner that the surfaces of the transparent electrode substrates having no photoanode layer may face each other.

[0048] The photoanode layers disposed on each of the two plate-type photoelectrodes may have the same thickness or a different thickness.

[0049] When the photoanode layers disposed on each of the two plate-type photoelectrode have the same thickness, the thickness of one photoanode may be preferably 500-700 nm, more preferably 550-650 nm, and most preferably 580-620 nm. When the thickness is smaller than 500 nm, it is not possible to utilize the irradiated light sufficiently. When the thickness is larger than 700 nm, the light arriving at the rear photoanode is reduced excessively, resulting in degradation of the overall light efficiency.

[0050] More preferably, the photoanode layers disposed on each of the two plate-type photoelectrodes may be formed to have a different thickness. Herein, the front photoanode layer receiving light irradiation directly may have a thickness of 50-450 nm, and the remaining rear photoanode layer may have a thickness of 600-1500 nm.

[0051] Preferably, the front photoanode layer may have a thickness of 100-350 nm, and the rear photoanode layer may have a thickness of 700-1300 nm. More preferably, the front photoanode layer may have a thickness of 150-300 nm, and the rear photoanode layer may have a thickness of 800-1000 nm. When the front photoanode and the rear photoanode have a thickness within the above-defined range, the light may be transferred well to the rear electrode, while using the light irradiated to the front electrode, thereby providing the highest light efficiency in the whole electrode.

[0052] The plate-type photoelectrode may be a square plate-type photoelectrode or a rectangular plate-type photoelectrode, and preferably may be a rectangular plate-type photoelectrode.

[0053] When the photoelectrode is fabricated in a rectangular shape, the migration distance of the electrons generated by the light and arriving at the transparent electrode is

relatively smaller as compared to a square photoelectrode, and thus a photoelectrode having a larger area can be manufactured. When using the photoelectrode in a plural number, the light reflected by the reflector may be transferred substantially to the whole surface of the rear side of the photoelectrode opposite to the side to which the light is irradiated, thereby providing significantly improved light efficiency. The square plate-type photoelectrode surface may have an area of 0.1-100 cm², preferably 0.3-50 cm², and more preferably 1-10 cm². When the area is smaller than 0.1 cm², a larger number of photoelectrodes is required based on the same area, which is inconvenient in manufacture and management. When the area is larger than 100 cm², the migration distance of the electrons generated by the light and arriving at the transparent electrode is increased to cause the problem of a decrease in number of electrons arriving at the transparent electrode through the recombination of electrons.

[0054] Meanwhile, the rectangular plate-type photoelectrode surface may have an area of 0.1-100 cm², preferably 0.3-50 cm², and more preferably 1-10 cm². When the area is smaller than 0.1 cm², a larger number of photoelectrodes is required based on the same area, which is inconvenient in manufacture and management. In the case of a rectangular shape, when the shorter side length is suitable for an electron migration distance, the longer side length may be increased with no limitation theoretically. However, an area of larger than 100 cm² is not preferred, considering the efficiency in manufacture or management, convenience, or the like. However, since the area of the rectangular plate-type photoelectrode is not directly related with the efficiency of the photoelectrode, except the problem in manufacture or management, the scope of the present disclosure is not limited to the above-defined area range, and the application thereof is not particularly limited.

[0055] The photoanode layer may have a ratio of width and length of 1:1-1:100, preferably 1:2-1:100, more preferably 1:10-1:50, and most preferably 1:20-1:30. When the ratio of width and length is decreased, the migration distance of the electrons generated by the light and arriving at the transparent electrode is increased, and thus the number of electrons arriving at the transparent electrode through the recombination of electrons may be reduced. When the ratio of width and length is increased excessively, the efficiency of manufacture or management may be reduced. Therefore, a ratio of width and length of 1:20-1:30 is most advantageous, considering the light efficiency or management efficiency.

[0056] The transparent electrode substrate may be any one selected from FTO, ZnO, ITO, AZO, GZO, IZO, and IGZO.

[0057] The photoanode layer may include any one selected from bismuth vanadate (BiVO₄), hematite (Fe₂O₃), and tungsten oxide (WO₃), and preferably may be bismuth vanadate (BiVO₄).

[0058] In another aspect of the present disclosure, there is provided a water splitting apparatus including the photoelectrochemical photoelectrode for water splitting.

[0059] Particularly, although it is not described clearly in the following examples, the photoelectrochemical photoelectrode for water splitting according to the present disclosure was determined in terms of its performance, while varying the number of photoelectrodes, shape and size of photoelectrodes, angle formed with the rear photoelectrode of the reflector, reflector material, interval between two

photoelectrodes, type of the transparent electrode substrate, and the type of the photoanode layer.

[0060] As a result, unlike the other conditions and the other numerical ranges, it is shown that the photoelectrode satisfying all of the following conditions provides the highest water splitting performance, when being applied to a water splitting apparatus.

[0061] The conditions include: the photoelectrode is provided in the form of a dual system; the photoelectrode has a rectangular shape; the angle formed between the rear side of the reflector and the photoelectrode is 8-12°; the reflector is made of a metal, particularly, silver (Ag); the interval between two photoelectrodes is 0.2-0.3 mm; the shorter side length of the rectangular photoelectrode surface is 0.2-0.3 cm, the area of the photoelectrode surface is not related directly with the efficiency, except the problem in manufacture and management; the transparent electrode substrate is FTO; and the photoanode layer uses bismuth vanadate (BiVO_4).

[0062] The examples and test examples will now be described. The following examples are for illustrative purposes only and not intended to limit the scope of this disclosure. It is apparent to those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the present disclosure, and such changes and modifications also fall within the scope of the disclosure as defined in the following claims.

EXAMPLES

Example 1

Dual Type+Reflector+Square Photoelectrode

[0063] Square BiVO_4 photoanode layers having the same area and a thickness of 600 nm were formed on a square FTO transparent electrode substrate having an area of 1 cm^2 and a thickness of 2 mm to obtain a photoelectrode. The two photoelectrodes were disposed in such a manner that they might face each other with an interval of 1 mm. In addition, the BiVO_4 photoanode layers in both of the photoelectrodes were allowed to face upwards so that the FTO transparent electrode substrate of the upper photoelectrode might face the BiVO_4 photoanode layer of the lower photoelectrode. Further, a reflector (1 $\text{cm} \times 1$ cm) made of a conventional mirror and having a thickness of 5 mm was installed in such a manner that it might form an angle of 30° with the photoelectrode surface on one surface of the BiVO_4 photoanode layer present at the side opposite to the light irradiation side, thereby providing a photoelectrochemical photoelectrode for water splitting.

Example 2

Dual Type+Reflector+Rectangular Photoelectrode

[0064] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 1, except that rectangular photoelectrodes having the same area (0.2 $\text{cm} \times 5.0$ cm) were used instead of the square photoelectrodes, and a reflector having a length (0.2 $\text{cm} \times 5.0$ cm) corresponding to the lateral length of the rectangular photoelectrode was used.

Example 3

Dual Type+Square Photoelectrode

[0065] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 1, except that the reflector was not used.

Example 4

Dual Type+Rectangular Photoelectrode

[0066] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 2, except that the reflector was not used.

Example 5

Dual Type+Reflector+Rectangular Photoelectrode (Photoanode Layer Position Adjusted)

[0067] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 2, except that the two photoelectrodes were disposed in such a manner that they might face each other and the FTO transparent electrode substrates of the upper photoelectrode and the lower photoelectrode might face each other (i.e. the BiVO_4 photoanode layer of the upper photoelectrode might face upwards and the BiVO_4 photoanode layer of the lower photoelectrode might face downwards).

Example 6

Dual Type+Rectangular Photoelectrode (Photoanode Layer Position Adjusted)

[0068] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 5, except that the reflector was not used.

Example 7

Dual Type+Reflector+Rectangular Photoelectrode (Photoanode Layer Thickness Adjusted)

[0069] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 5, except that the BiVO_4 photoanode layer of the upper photoelectrode was formed to have a thickness of 200 nm, and the BiVO_4 photoanode layer of the lower photoelectrode was formed to have a thickness of 600 nm.

Example 8

Dual Type+Reflector+Rectangular Photoelectrode (Photoanode Layer Thickness Adjusted)

[0070] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 7, except that the BiVO_4 photoanode layer of the lower photoelectrode was formed to have a thickness of 900 nm.

Example 9

Dual the+Reflector+Rectangular Photoelectrode (Photoanode Layer Thickness Adjusted)

[0071] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 7,

except that the BiVO₄ photoanode layer of the lower photoelectrode was formed to have a thickness of 1500 nm.

Example 10

Dual Type+Rectangular Photoelectrode
(Photoanode Layer Thickness Adjusted)

[0072] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 4, except that the BiVO₄ photoanode layers of the upper and the lower photoelectrodes were formed to have a thickness of 200 nm.

Example 11

Dual Type+Rectangular Photoelectrode
(Photoanode Layer Thickness Adjusted)

[0073] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 4, except that the BiVO₄ photoanode layers of the upper and the lower photoelectrodes were formed to have a thickness of 900 nm.

Example 12

Dual Type+Rectangular Photoelectrode
(Photoanode Layer Thickness Adjusted)

[0074] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Example 4, except that the BiVO₄ photoanode layers of the upper and the lower photoelectrodes were formed to have a thickness of 1500 nm.

Comparative Example 1

Single Type+Square Photoelectrode

[0075] A photoelectrode was obtained in the same manner as Example 3, except that only one square photoelectrode was used.

Comparative Example 2

Single Type+Square Photoelectrode

[0076] A photoelectrode was obtained in the same manner as Comparative Example 1, except that a laboratory scale photoelectrode defined by National Renewable Energy Laboratory (NREL) and having an area of 0.3 cm×0.3 cm=0.09 cm² was used instead of the square photoelectrode having an area of 1 cm².

Comparative Example 3

Single Type+Rectangular Photoelectrode

[0077] A photoelectrode was obtained in the same manner as Example 4, except that only one rectangular photoelectrode was used.

Comparative Example 4

Dual Type+Rectangular Photoelectrode
(Photoanode Layer Thickness Adjusted)

[0078] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Comparative Example 3, except that the BiVO₄ photoanode layer was formed to have a thickness of 200 nm.

Comparative Example 5

Dual Type+Rectangular Photoelectrode
(Photoanode Layer Thickness Adjusted)

[0079] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Comparative Example 3, except that the BiVO₄ photoanode layer was formed to have a thickness of 900 nm.

Comparative Example 6

Dual Type+Rectangular Photoelectrode
(Photoanode Layer Thickness Adjusted)

[0080] A photoelectrochemical photoelectrode for water splitting was obtained in the same manner as Comparative Example 3, except that the BiVO₄ photoanode layer was formed to have a thickness of 1500 nm.

[0081] The schematic structure of the photoelectrode (a) according to Example 1 and that of the photoelectrode (b) according to Example 2 are shown in FIGS. 1A and 1B. In addition, the schematic structures of the square photoelectrodes (a) according to Comparative Examples 1 and 2 and those of the rectangular photoelectrodes (b) according to Comparative Examples 3-6 are shown in FIGS. 2A and 2B.

[0082] Further, the constitution of each of the photoelectrodes according to Examples 1-12 and Comparative Examples 1-6 is summarized and shown in Table 1.

TABLE 1

Photoelectrode		Photoelectrode (photoanode) area	Number of	Photoanode thickness (nm)		Photoanode position of lower	Presence of
	shape	(cm ²)/electrode	photoelectrodes	Upper	Lower	photoelectrode	reflector
Ex. 1	Square	1	2	600	600	Upwards	Yes
Ex. 2	Rectangular	1	2	600	600	Upwards	Yes
Ex. 3	Square	1	2	600	600	Upwards	No
Ex. 4	Rectangular	1	2	600	600	Upwards	No
Ex. 5	Rectangular	1	2	600	600	Downwards	Yes
Ex. 6	Rectangular	1	2	600	600	Downwards	No

TABLE 1-continued

		Photoelectrode (photoanode) area	Number of	Photoanode thickness (nm)		Photoanode position of lower	Presence of
	Photoelectrode shape	(cm ²)/electrode	photoelectrodes	Upper	Lower	photoelectrode	reflector
Ex. 7	Rectangular	1	2	200	600	Downwards	Yes
Ex. 8	Rectangular	1	2	200	900	Downwards	Yes
Ex. 9	Rectangular	1	2	200	1500	Downwards	Yes
Ex. 10	Rectangular	1	2	200	200	Upwards	No
Ex. 11	Rectangular	1	2	900	900	Upwards	No
Ex. 12	Rectangular	1	2	1500	1500	Upwards	No
Comp. Ex. 1	Square	1	1		600	Upwards	No
Comp. Ex. 2	Square	0.09	1		600	Upwards	No
Comp. Ex. 3	Rectangular	1	1		600	Upwards	No
Comp. Ex. 4	Rectangular	1	1		200	Upwards	No
Comp. Ex. 5	Rectangular	1	1		900	Upwards	No
Comp. Ex. 6	Rectangular	1	1		1500	Upwards	No

TEST EXAMPLES

Test Example 1

Analysis of Water Splitting Performance Depending
on Area of Photoelectrochemical Electrode

[0083] The square BiVO₄ photoelectrodes according to Comparative Example 1 (area=1 cm²) and Comparative Example 2 (area=0.09 cm²) were tested in terms of water splitting performance depending on area. In the water splitting performance test, the light of solar simulator 1 SUN was used, and each of the electrodes was used as a working electrode, Pt mesh was used as a counter electrode and an Ag/AgCl electrode was used as a reference electrode to calculate the photoelectric current density based on a reversible hydrogen electrode (RHE). In addition, 0.2 M borate buffer solution was used as an electrolyte, and a small amount of Na₂CO₃ functioning as a hole scavenger capable of preventing recombination was added thereto in order to maximize hydrogen generation.

[0084] The result of the water splitting performance analysis according to the above-mentioned method is shown in FIG. 3. It can be seen that the photoelectrode having a smaller area (=0.09 cm²) according to Comparative Example 2 shows a higher photoelectric current density, while the photoelectrode having a relatively larger area (=1 cm²) according to Comparative Example 1 shows a decrease in photoelectric current density. Photoelectrochemistry (PEC) can proceed hydrogen generation, when the electrons produced from a semiconductor material by the light arrives at a platinum (Pt) catalyst through an FTO transparent electrode. However, as shown in the front views of the electrodes according to Comparative Examples 1 and 2 of FIG. 3, the smaller photoelectrode allows the electrons produced by the light to arrive rapidly at the FTO transparent electrode, while the photoelectrode having a larger area requires a relatively increased migration distance in order to allow the electrons produced by the light to arrive at the FTO transparent electrode.

[0085] When the electron migration distance is increased as mentioned above, a possibility of recombination of hydrogen with oxygen is increased, resulting in a significant decrease in the amount of electron arriving at the FTO transparent electrode, as compared to the electrons produced by the light. Therefore, it is necessary to study a photoelectrode with a design that can reduce the migration distance of electrons while making the area of the photoelectrode larger.

Test Example 2

Analysis of Water Splitting Performance Depending
on Photoelectrode Shape

[0086] To determine a difference in water splitting performance depending on the shape of a photoelectrode, the same square-shaped photoelectrodes or the photoelectrodes having a different shape according to Comparative Example 1 (square) and

[0087] Comparative Example 3 (rectangular) were tested in the same manner as Test Example 1. The result is shown in FIGS. 4A and 4B. FIG. 4A illustrates the result of comparison of Comparative Example 1 with Comparative Example 3, and FIG. 4B illustrates the result of comparison of the photoelectric current density of each of Comparative Examples 1 and 3 with that of the photoelectrode having a smaller area according to Comparative Example 2.

[0088] As shown in FIG. 4A, the rectangular photoelectrode according to Comparative Example 3 shows higher water splitting performance as compared to the square photoelectrode according to Comparative Example 1 in the whole voltage region. This is because the rectangular photoelectrode provides a minimized migration distance of the electrons produced by the light and arriving at the FTO transparent electrode, and thus shows improved water splitting performance, as shown in FIGS. 2A and 2B. In addition, as shown in FIG. 4B, the water splitting performance of the rectangular photoelectrode according to Comparative Example 3 is not degraded significantly as compared to the square photoelectrode having a smaller area according to Comparative Example 2. In other words, although the photo-

photoelectrode according to Comparative Example 3 has an area approximately 10 times ($0.09 \text{ cm}^2 \rightarrow 1 \text{ cm}^2$) higher than the area of the photoelectrode according to Comparative Example 2, it shows a significantly small decrease in photoelectric current density. This suggests that a rectangular photoelectrode is a significantly advisable design in scale-up of a photoelectrode.

Test Example 3

Analysis of Water Splitting Performance of Photoelectrode Depending on Number and Shape of Photoelectrodes and Presence of Reflector

[0089] To analyze the water splitting performance of a photoelectrode depending on the number and shape of photoelectrodes and the presence of a reflector, a test was carried out in the same manner as Test Example 1. The result is shown in FIGS. 5A to 5C.

[0090] Herein, FIG. 5A illustrates the result of comparison of the square photoelectrodes (1 cm^2) with one another, wherein the photoelectrode with a single system using one photoelectrode according to Comparative Example 1, the photoelectrode with a dual system using two photoelectrodes according to Example 3, and the photoelectrode with a dual system and further using a reflector according to Example 1 are tested. As shown in FIG. 5A, since Example 3 with a dual system generates more electrons as compared to Comparative Example 1 with a single system, Example 3 shows higher water splitting performance. In addition, in the case of Example 1 with a dual system and further using a reflector, the light is supplied efficiently even to the photoelectrode disposed at the side opposite to the light irradiation direction and not receiving the irradiated light directly, and thus the photoelectrode according to Example 1 shows higher photoelectric current as compared to Example 3 including no reflector.

[0091] FIG. 5B illustrates the result of comparison of the rectangular photoelectrodes (1 cm^2) with one another, wherein the photoelectrode with a single system using one photoelectrode according to Comparative Example 3, the photoelectrode with a dual system using two photoelectrodes according to Example 4, and the photoelectrode with a dual system and further using a reflector according to Example 2 are tested. As shown in FIG. 5B, when using a rectangular photoelectrode, Example 4 with a dual system shows a significantly large increase in photoelectric current density as compared to Comparative Example 3 with a single system. In addition, it can be seen that Example 2 with a dual system and including a reflector shows a significantly larger increase in photoelectric current density as compared to the square photoelectrode of Example 1 under the same conditions. This is because the light is supplied efficiently even to the rectangular photoelectrode disposed at the side opposite to the light irradiation direction and not receiving the irradiated light directly, and the migration distance of the electrons produced by the light and arriving at the FTO transparent electrode is short, in the case of Example 2, and thus Example 2 shows a significantly large increase in photoelectric current density.

[0092] FIG. 5C illustrates the test results of Examples 1 and 2 using two photoelectrodes, including a reflector and having a different photoelectrode shape. As shown in FIG. 5C, the square photoelectrode according to Example 1 shows a photoelectric current density of 6.25 mA cm^{-2} at

1.23 V vs. RHE , while the rectangular photoelectrode according to Example 2 shows a photoelectric current density of 7.93 mA cm^{-2} . In other words, it can be seen that the rectangular photoelectrode shows higher water splitting performance as compared to the square photoelectrode. As a result, it can be seen that when a photoelectrode satisfies all of the conditions of a rectangular shape, a dual system and use of a reflector, it shows the highest water splitting performance.

[0093] The photoelectrode according to the present disclosure is a transparent electrode, and thus the upper photoelectrode receives the light and the transmitted light may be used for the photoelectrode disposed at the side opposite to the light irradiation side. In addition, when using a reflector additionally, the lower photoelectrode also can absorb the light efficiently. Meanwhile, in the case of the square photoelectrode, the size of a reflector is limited, and thus it is difficult to supply the light to the whole position of the lower photoelectrode surface. On the contrary, when using the rectangular photoelectrodes in a dual system, the photoelectrode has a small width, and thus the light reflected by the reflector can be transferred to the whole position of the lower photoelectrode surface, thereby providing significantly improved light efficiency.

Test Example 4

Analysis of Water Splitting Performance Depending on Photoanode Position

[0094] To analyze the water splitting performance of a photoelectrode depending on the position of a photoanode, a test was carried out in the same manner as Test Example 1.

[0095] FIG. 6 shows the structure of the photoelectrochemical photoelectrode according to Example 2 as compared to that of the photoelectrochemical photoelectrode according to Example 5, wherein the position of the photoanode of the lower electrode in Example 2 is opposite to the position of the photoanode of the lower electrode in Example 5. It can be seen that the position of the photoanode in the lower electrode of the photoelectrode according to Example 5 is opposite to the position of the photoanode in Example 2 and is designed to face the reflector.

[0096] FIGS. 7A to 7C illustrate the result of determination of the electrode efficiency according to this Test Example.

[0097] Herein, FIG. 7A illustrates the results of comparison of the efficiency of the front electrode, the rear electrode and the whole electrode according to Example 2.

[0098] In addition, FIG. 7B shows the electrode efficiency of each of the lower electrodes according to Examples 2 and 5 including a photoanode at a different position of the lower electrode in the photoelectrode. As shown in FIG. 7B, the lower electrode including a photoanode formed at the opposite side as compared to the upper electrode and facing the reflector shows higher electrode efficiency.

[0099] Further, FIG. 7C illustrates the result of comparison of electrode efficiency between the whole photoelectrode according to Example 5 and the whole photoelectrode according to Example 6. As shown in FIG. 7C, both photoelectrodes include a photoanode formed downwards in the lower electrode, but the photoelectrode provided with a reflector according to Example 5 shows higher electrode efficiency.

[0100] In other words, the photoelectrode including a photoanode formed downwards in the lower electrode and provided with a reflector according to Example 5 shows the highest electrode efficiency.

Test Example 5

Analysis of Water Splitting Performance Depending on Photoanode Thickness

[0101] To analyze the water splitting performance depending on the thickness of a photoanode of photoelectrode, a test was carried out in the same manner as Test Example 1. The result is shown in FIGS. 8A to 8D. Herein, all of the photoelectrodes have a rectangular shape (0.2 cm×5 cm). In the case of a dual system, the photoanodes of the upper electrode and the lower electrode have the same thickness. Particularly, FIG. 8A shows the result of a photoanode having a thickness of 200 nm, FIG. 8B shows the result of a photoanode having a thickness of 600 nm, FIG. 8C shows the result of a photoanode having a thickness of 900 nm, and FIG. 8D shows the result of a photoanode having a thickness of 1500 nm.

[0102] It can be seen that the photoanode having a thickness of 900 nm according to Comparative Example 5 shows the highest efficiency, in the case of a single-system photoelectrode, while the photoanode having a thickness of 600 nm according to Example 4 shows the highest efficiency, in the case of a dual-system photoelectrode. In the case of a dual-system photoelectrode, it can be seen that when the upper electrode has an excessively large thickness, the lower electrode cannot use the light efficiently.

Test Example 6

Analysis of Water Splitting Performance Depending on Change in Photoanode Thickness

[0103] In the dual-system photoelectrochemical photoelectrode according to the present disclosure, the water splitting performance of the photoelectrodes using a photoanode having a different thickness for the upper electrode and the lower electrode according to each of Examples 7-9 was analyzed. The result is shown in FIGS. 9A to 9C.

[0104] As shown in FIGS. 9A to 9C, the dual-system photoelectrode including an upper photoanode having a thickness of 200 nm and a lower photoanode having a thickness of 900 nm according to Example 8 shows the highest electrode efficiency.

[0105] In other words, when the photoelectrochemical photoelectrode for water splitting according to the present disclosure is a dual system, includes an upper photoanode having a thickness of 200 nm and a lower photoanode having a thickness of 900 nm, and is further provided with a reflector, it shows the highest electrode efficiency.

[0106] While the present disclosure has been described with respect to the specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made by addition, change or elimination of constitutional elements without departing from the spirit and scope of the disclosure as defined in the following claims, and such changes and modifications also fall within the scope of the present disclosure.

What is claimed is:

1. A photoelectrochemical photoelectrode for water splitting, which comprises a plate-type photoelectrode compris-

ing a transparent electrode substrate and a photoanode layer disposed on the transparent electrode substrate, wherein the plate-type photoelectrode exists in a plural number, and the plural plate-type photoelectrodes are spaced apart from each other by a predetermined interval so that they may be disposed face-to-face.

2. The photoelectrochemical photoelectrode for water splitting according to claim 1, which further comprises a reflector which reflects the light transmitted through all of the plural photoelectrodes toward a rear photoelectrode side opposite to a front photoelectrode receiving light irradiation directly, upon the light irradiation.

3. The photoelectrochemical photoelectrode for water splitting according to claim 2, wherein the reflector is disposed in the shape of a plate along one side of the rear photoelectrode.

4. The photoelectrochemical photoelectrode for water splitting according to claim 3, wherein the reflector is installed to form an angle of 3-45° with the rear photoelectrode.

5. The photoelectrochemical photoelectrode for water splitting according to claim 2, wherein the reflector comprises any one material selected from glass, crystal, halite, metals and polymers.

6. The photoelectrochemical photoelectrode for water splitting according to claim 1, which comprises two plate-type photoelectrodes.

7. The photoelectrochemical photoelectrode for water splitting according to claim 6, wherein the two plate-type photoelectrodes are disposed in such a manner that the surfaces of the transparent electrode substrates having no photoanode layer may face each other.

8. The photoelectrochemical photoelectrode for water splitting according to claim 6, wherein the photoanode layers disposed on each of the two plate-type photoelectrodes have the same thickness and are formed to have a thickness of 500-700 nm.

9. The photoelectrochemical photoelectrode for water splitting according to claim 6, wherein the photoanode layers disposed on each of the two plate-type photoelectrodes have a different thickness, wherein the front photoanode layer receiving light irradiation directly has a thickness of 50-450 nm, and the remaining rear photoanode layer has a thickness of 600-1500 nm.

10. The photoelectrochemical photoelectrode for water splitting according to claim 6, wherein the two plate-type photoelectrodes are disposed in such a manner that they may be spaced apart from each other by an interval of 0.1-1.0 mm.

11. The photoelectrochemical photoelectrode for water splitting according to claim 1, wherein the plate-type photoelectrode is a square plate-type photoelectrode or a rectangular plate-type photoelectrode.

12. The photoelectrochemical photoelectrode for water splitting according to claim 1, wherein the photoanode layer has a ratio of width and length of 1:1-1:100.

13. The photoelectrochemical photoelectrode for water splitting according to claim 1, wherein the transparent electrode substrate is any one selected from FTO, ZnO, ITO, AZO, GZO, IZO, and IGZO.

14. The photoelectrochemical photoelectrode for water splitting according to claim 1, wherein the photoanode layer comprises any one selected from bismuth vanadate (BiVO₄), hematite (Fe₂O₃), and tungsten oxide (WO₃).

15. A water splitting apparatus comprising the photoelectrochemical photoelectrode for water splitting as defined in claim 1.

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